

DO NOT ENTER: /JC/

# EXHIBIT A

---

# PRINCIPLES OF POLYMERIZATION

---

Third Edition

**GEORGE ODIAN**

The College of Staten Island  
The City University of New York  
Staten Island, New York



A Wiley-Interscience Publication

**JOHN WILEY & SONS, INC.**

New York / Chichester / Brisbane / Toronto / Singapore



In recognition of the importance of preserving what has been written, it is a policy of John Wiley & Sons, Inc., to have books of enduring value published in the United States printed on acid-free paper, and we exert our best efforts to that end.

Copyright © 1991 by John Wiley & Sons, Inc.

All rights reserved. Published simultaneously in Canada.

Reproduction or translation of any part of this work beyond that permitted by Section 107 or 108 of the 1976 United States Copyright Act without the permission of the copyright owner is unlawful. Requests for permission or further information should be addressed to the Permissions Department, John Wiley & Sons, Inc.

***Library of Congress Cataloging in Publication Data:***

Odian, George G., 1933–

Principles of polymerization / George Odian.—3rd ed.

p. cm.

“A Wiley-Interscience publication.”

Includes index.

ISBN 0-471-61020-8

1. Polymerization. I. Title.

QD281.P603 1991

541.3'93—dc20

90-24785  
CIP

Printed in the United States of America

10 9 8

## PREFACE

This book describes the physical polymer molecules are synthesized reader to the characteristics that c homologs (Chap. 1) and then pro of polymerization reactions—step. 2–5, 7). Polymerization reactions thermodynamic features, their sco polymer structures, and the proce Polymer chemistry has advanced to a variety of different types of polym. Emphasis is placed throughout the are important in controlling polym. tural features such as branching an reader an appreciation of the vers and that is available to the synthe

The versatility of polymerization: that can be polymerized but also : stereospecific polymerization. Cha copolymerization and is considere are discussed in the appropriate ch polymerization with emphasis on t tures by the appropriate choice of p 9), the reactions of polymers that a structures and the use of polymeri The literature has been covered th

This book is intended for chem experienced polymer chemist. The polymers for the former. Each topi

not alter the  $\frac{2}{3}$ -power dependence of mechanism indicates a more complex process monotonically from 1.2 to 0.4. Particle size is higher and the nucleation concentrations. Polymer particle formation is a greater tendency for capture at the latter concentrations are high. Eq. 4-11, there is compatibility with the  $\frac{2}{3}$ -Eq. 4-10.

tendency toward radical desorption, on  $S$  and  $R_i$ , respectively. This result, nucleation since one cannot preclude larger and smaller, respectively, than those studied. Monomers such as Case 1 behavior, tend to show a by Eq. 4-11, indicating the presence of dependence of  $N$  on  $R_i$  deviates markedly. Desorption occurs, the large fraction of the result that  $N$  is little affected by is 0.64 for styrene, 0.86 for methyl or vinyl acetate, while the orders of activity [Hansen and Ugelstad, 1979a, acrylonitrile and butyl acrylate shows a and  $S$  from 0.67 to 0.40 with increasing surfactant was used [Capek et al., 1988]. Reaction in the presence of a cationic sur-

face emulsion polymerizations—inverse concentration. Some surfactants act as catalysts of the more highly reactive radicals [Motoyama, 1962; Stryker et al., 1962], possessing unsaturation (e.g., certain allyl hydrogens is probably quite

during Intervals II and III since the total coverage of the surface with surfactant appears to be insufficient to cause nucleation since  $N$  is generally observed to be constant. Activity decreases sufficiently to cause the transition [Blackley, 1975].

## EMULSION POLYMERIZATION

are water-soluble initiators such as hydrogen peroxide, and 2,2'-azobis(2-amidinobenzene) peroxides such as succinic acid peroxides such as 4,4'-azobis(4-cyanopen- tane) diamine such as persulfate with ferrous ion

(Eq. 3-38a) are commonly used. Redox systems are advantageous in yielding desirable initiation rates at temperatures below 50°C. Other useful redox systems include cumyl hydroperoxide or hydrogen peroxide with ferrous, sulfite, or bisulfite ion.

### 4-3b Surfactants

Anionic surfactants are the most commonly used surfactants in emulsion polymerization [Blackley, 1975; Gardon, 1977]. These include fatty acid soaps (sodium or potassium stearate, laurate, palmitate), sulfates, and sulfonates (sodium lauryl sulfate and sodium dodecylbenzene sulfonate). The sulfates and sulfonates are useful for polymerization in acidic medium where fatty acid soaps are unstable or where the final product must be stable toward either acid or heavy-metal ions. Nonionic surfactants such as poly(ethylene oxide), poly(vinyl alcohol) and hydroxyethyl cellulose are sometimes used in conjunction with anionic surfactants for improving the freeze-thaw and shear stability of the polymer or to aid in controlling particle size and size distribution. The presence of the nonionic surfactant imparts a second mode of colloidal stabilization, in addition to electrostatic stabilization by the anionic surfactant, via steric interference with the van der Waals attraction between polymer particles. Nonionic surfactants are also of use where the final polymer latex should be insensitive to changes in pH over a wide range. Nonionic surfactants are only infrequently used alone, since their efficiency in producing stable emulsions is less than that of the anionic surfactants. Anionic surfactants are generally used at a level of 0.2–3 wt % based on the amount of water; nonionic surfactants are used at the 2–10% level. Cationic surfactants such as dodecylammonium chloride and cetyltrimethylammonium bromide are much less frequently used than anionic surfactants because of their inefficient emulsifying action or adverse effects on initiator decomposition. Also, cationic surfactants are more expensive than anionic surfactants.

Surfactants increase particle number and decrease particle size as their concentration in the initial reaction charge is increased. However, one can use delayed addition of surfactant after nucleation is complete to improve particle stability, without affecting the particle number, size, and size distribution.

### 4-3c Other Components

The quality of the water used in emulsion polymerization is important. Deionized water may be used since the presence of foreign ions or ions in uncontrolled concentrations can interfere with both the initiation process and the action of the emulsifier. Antifreeze additives are used to allow polymerization at temperatures below 0°C. These include inorganic electrolytes as well as organics such as ethylene glycol, glycerol, methanol, and monoalkyl ethers of ethylene glycol. The addition of inorganic electrolytes often affects the polymerization rate and stability of the emulsion. Sequestering agents such as ethylenediamine tetraacetic acid or its alkali metal salts may be added to help solubilize a component of the initiator system or to deactivate traces of calcium and magnesium ions present in the water. Buffers such as phosphate or citrate salts may be used to stabilize the latex toward pH changes.

### 4-3d Propagation and Termination Rate Constants

Emulsion polymerization proceeds in a polymer particle where the concentration of polymer is quite high throughout the reaction. This type of system is then similar to

DO NOT ENTER: /JC/